

Nitrogen doping of Al- and Ti-phosphate through plasma-enhanced ALD

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Phosphates have shown to be promising materials for Li-ion battery (LIB) applications. Their applications vary from protective coatings (Al-phosphate^[1,2]) to potential cathode materials (Ti-phosphate^[3]). Using ALD to tune the ionic and/or electronic conductivity through in-situ N-doping could make these materials even more interesting. In order to, for example, decrease the ionic and electronic blocking effect of the protective Al-phosphate coating, a new plasma enhanced atomic layer deposition (PE-ALD) process has been investigated. This new process is based on reports on PE-ALD of metal phosphates using a combination of trimethyl phosphate plasma (TMP*), oxygen plasma (O₂*) and a metal precursor (TMA or TTIP)^[3,4].

In combining a nitrogen-containing phosphorous precursor, i.e. diethyl phosphoramidate plasma (DEPA*), with nitrogen plasma (N₂*) and TMA/TTIP, a large GPC of 1.5 nm/cycle for N-doped Al-phosphate and 0.5 nm/cycle for N-doped Ti-phosphate was obtained. For both phosphates, self-limited growth is observed (figure 1, 2), and N-doping of respectively 7.9 at.% and 8.6 at.% for Al-phosphate and Ti-phosphate was found with Elastic Recoil Detection (ERD) (figure 3).

A clear effect of the nitrogen doping on the effective transversal ionic and electronic conductivities is observed (figure 4a). For both phosphates, a significant increase in the effective electronic conductivity is found. This is important, as phosphates (such as Fe-phosphate) typically suffer from poor electronic conductivity. The effective ionic conductivity shows a small increase for the Al-phosphate, but a slight decrease for Ti-phosphate. To study the possibilities of N-doped Al-phosphate in particular, a lithium nickel manganese cobalt oxide (NMC) powder was coated with (N-doped) Al-phosphate. An improved energy density at high discharge rates (w.r.t. uncoated NMC) was observed after only one deposition cycle of N-doped Al-phosphate, while the blocking effect of the undoped Al-phosphate coating (with a similar thickness as N-doped Al-phosphate) showed to hamper the battery performance at high rates (figure 4b). This shows that N-doping of phosphates with a high GPC was achieved by a new PE-ALD process, opening up opportunities for improving different types of phosphate coatings for LIB applications.

[1] Cho, J. et al., Journal of The Electrochemical Society, A1899-A1904 (2004).

[2] Cho, J. et al., Angewandte Chemie International Edition, 1618-1621 (2003).

[3] Dobbelaere, T. et al., J. Mater. Chem. A 5, 330 (2017).

[4] Dobbelaere, T. et al., Chem. Mater. 6863–6871 (2014).

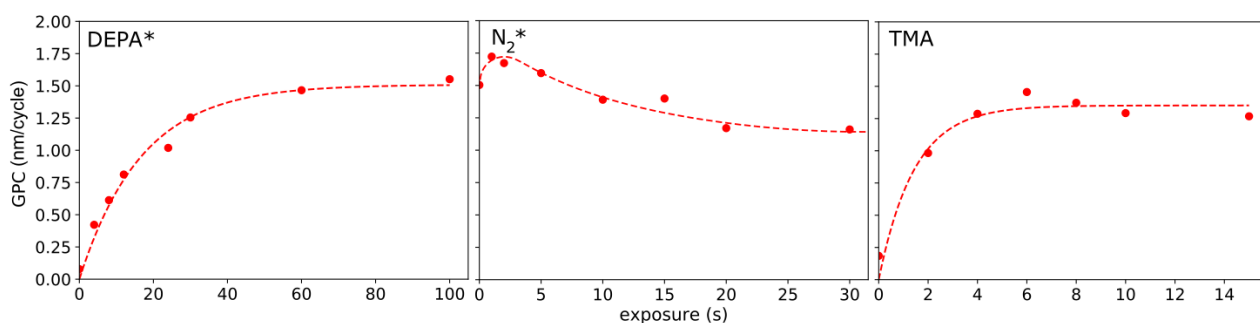


Figure 1. Saturation of DEPA*, N₂* and TMA steps during PE-ALD of N-doped Al-phosphate.

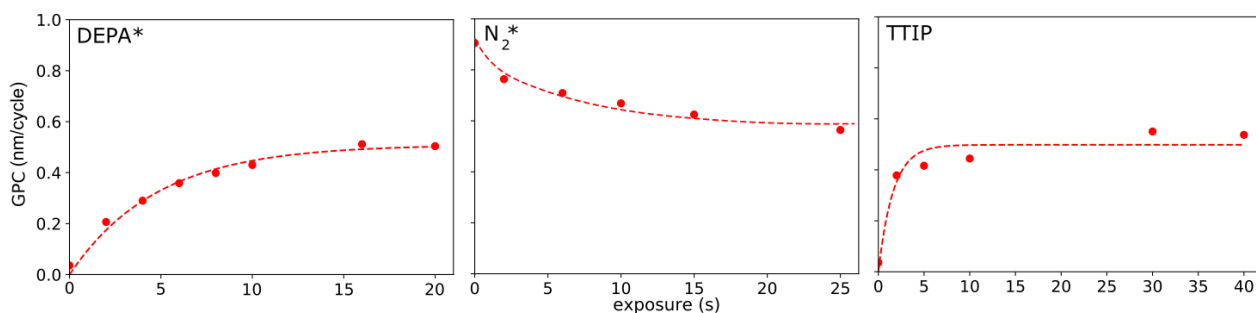


Figure 2. Saturation of DEPA*, N₂* and TTIP steps during PE-ALD of N-doped Ti-phosphate.

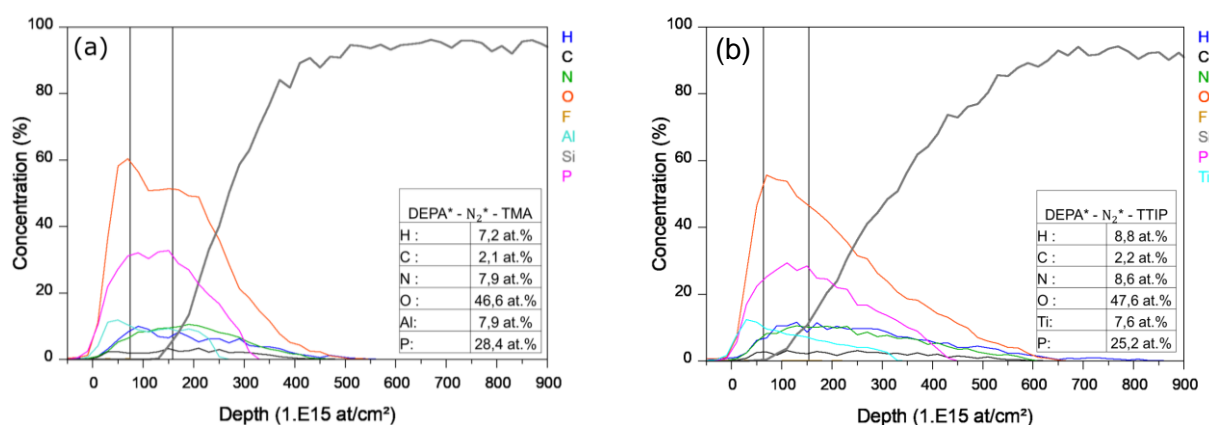


Figure 3. Atomic concentrations of (a) N-doped Al-phosphate and (b) N-doped Ti-phosphate.

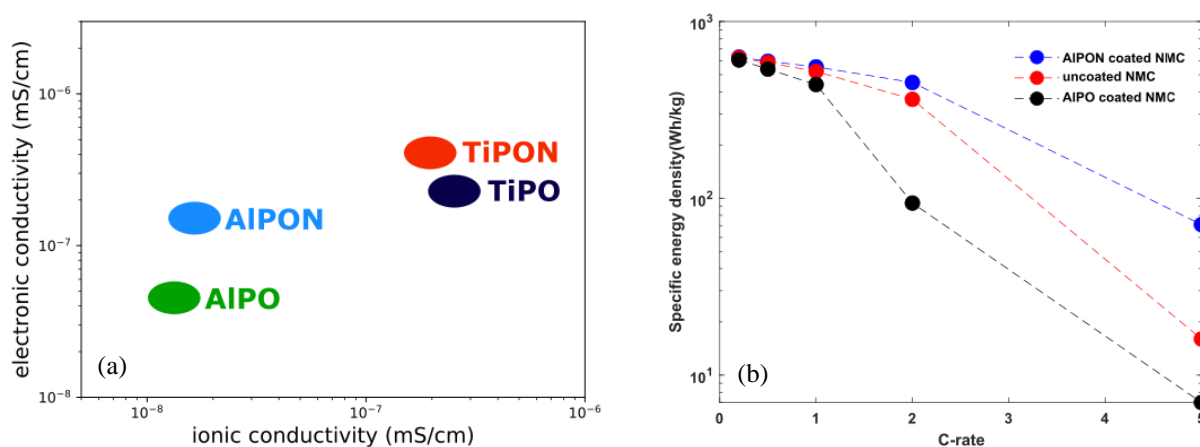


Figure 4. (a) Effect of nitrogen doping on ionic and electronic conductivity of a thin film coating and (b) the effect an (N-doped) Al-phosphate coating on the kinetics of NMC. AIPON and TiPON refer to N-doped Al- and Ti-phosphate, while AIPO and TiPO refer to undoped Al- and Ti-phosphate. A C-rate of 1 means that a current is applied to (dis)charge the electrode's theoretical capacity in 1 hour. A C-rate of 10, indicates (dis)charging in 1/10 of an hour.